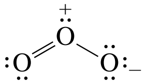
I have highlighted in yellow and annotated in red. ADH

1.9 RESONANCE

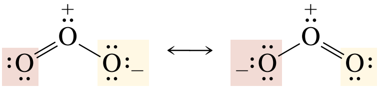
When writing a Lewis structure, we restrict a molecule's electrons to certain well-defined locations, either linking two atoms by a covalent bond or as unshared electrons on a single atom. Sometimes more than one Lewis structure can be written for a molecule, especially those that contain multiple bonds. An example often cited in introductory chemistry courses is ozone (O_3). Ozone occurs naturally in large quantities in the upper atmosphere, where it screens the surface of the earth from much of the sun's ultraviolet rays. Were it not for this ozone layer, most forms of surface life on earth would be damaged or even destroyed by the rays of the sun. The following Lewis structure for ozone satisfies the octet rule; all three oxygens have 8 electrons in their valence shell.



Bond distances in organic compounds are usually 1 to 2Å (1Å = 10^{-10}m). Since the angstrom (Å) is not an SI unit, we will express bond distances in picometers (1 pm = 10^{-12}m). Thus, 128 pm = 1.28 Å.

This Lewis structure, however, doesn't accurately portray the bonding in ozone, because the two terminal oxygens are bonded differently to the central oxygen. The central oxygen is depicted as doubly bonded to one and singly bonded to the other. Since it is generally true that double bonds are shorter than single bonds, we would expect ozone to exhibit two different O—O bond lengths, one of them characteristic of the O—O single bond distance (147 pm in hydrogen peroxide, H—O—O—H) and the other one characteristic of the O═O double bond distance (121 pm in O_2). Such is not the case. Both bond distances in ozone are exactly the same (128 pm)—somewhat shorter than the single bond distance and somewhat longer than the double bond distance. The structure of ozone requires that *the central oxygen must be identically bonded to both terminal oxygens.*

In order to deal with circumstances such as the bonding in ozone, the notion of **resonance** between Lewis structures was developed. According to the resonance concept, when more than one Lewis structure may be written for a molecule, a single structure is not sufficient to describe it. Rather, the true structure has an electron distribution that is a "hybrid" of all the possible Lewis structures that can be written for the molecule. In the case of ozone, two equivalent Lewis structures may be written. We use a double-headed arrow to represent resonance between these two Lewis structures.

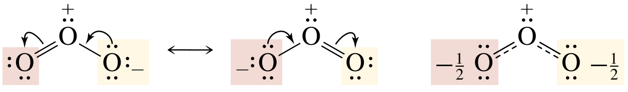


It is important to remember that the double-headed resonance arrow does not indicate a *process* in which the two Lewis structures interconvert. Ozone, for example, has a *single* structure; it does not oscillate back and forth between two Lewis structures, rather its true structure is not adequately represented by any single Lewis structure.

Resonance attempts to correct a fundamental defect in Lewis formulas. Lewis formulas show electrons as being **localized;** they either are shared between two atoms in a covalent bond or are unshared electrons belonging to a single atom. In reality, electrons distribute themselves in the way that leads to their most stable arrangement. This sometimes means that a pair of electrons is **delocalized,** or shared by several nuclei. What we try to show by the resonance description of ozone is the delocalization of the lone-pair electrons of one oxygen and the electrons in the double bond over the three atoms of the molecule. Organic chemists often use curved arrows to show this electron

[omit the dashed-line notation]

delocalization. [Alternatively, an average of two Lewis structures is sometimes drawn using a dashed line to represent a "partial" bond. In the dashed-line notation the central oxygen is linked to the other two by bonds that are halfway between a single bond and a double bond, and the terminal oxygens each bear one half of a unit negative charge.]



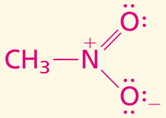
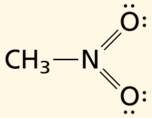
Curved arrow notation Dashed-line notation

Electron delocalization in ozone

we will not use this dashed-line notation

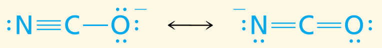
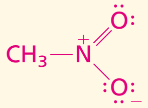
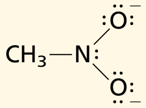
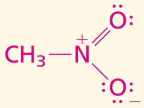
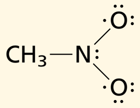
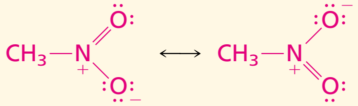
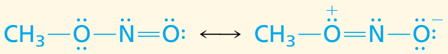
The rules to be followed when writing resonance structures are summarized in Table 1.5.

TABLE 1.5 Introduction to the Rules of Resonance

Rule	Illustration
1. Atomic positions (connectivity) must be the same in all resonance structures; only the electron positions may vary among the various contributing structures. Do not move atoms, only electrons are moved	The structural formulas  A and $CH_3-\ddot{O}-\ddot{N}=\ddot{O}:$ B represent different compounds, not different resonance forms of the same compound. A is a Lewis structure for *nitromethane;* B is *methyl nitrite.*
2. Lewis structures in which second-row elements own or share more than 8 valence electrons are especially unstable and make no contribution to the true structure. (The octet rule may be exceeded for elements beyond the second row.) *d* electrons first appear when $n = 3$	Structural formula C,  C has 10 electrons around nitrogen. It is not a permissible Lewis structure for nitromethane and so cannot be a valid resonance form.
3. When two or more structures satisfy the octet rule, the most stable one is the one with the smallest separation of oppositely charged atoms. In the case when valence shell expansion is employed, the preferred set of resonance structures are those which minimize charge separation while maximizing the number of resonance structures.	The two Lewis structures D and E of methyl nitrite satisfy the octet rule: $CH_3-\ddot{O}-\ddot{N}=\ddot{O}: \longleftrightarrow CH_3-\overset{+}{\ddot{O}}=\ddot{N}-\ddot{O}:^{-}$ D E Structure D has no separation of charge and is more stable than E, which does. The true structure of methyl nitrite is more like D than E.

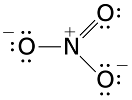
(Continued)

TABLE 1.5 Introduction to the Rules of Resonance ***(Continued)***

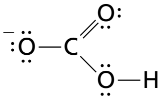
Rule	Illustration
4. Among structural formulas in which the octet rule is satisfied for all atoms and one or more of these atoms bears a formal charge, the most stable resonance form is the one in which negative charge resides on the most electronegative atom (or positive charge on the most electropositive one).	The most stable Lewis structure for cyanate ion is F because the negative charge is on its oxygen.  $:N\equiv C-\ddot{\underset{..}{O}}:^- \longleftrightarrow {}^-:\underset{..}{N}=C=\underset{..}{O}:$ F G In G the negative charge is on nitrogen. Oxygen is more electronegative than nitrogen and can better support a negative charge.
5. Each contributing Lewis structure must have the same number of electrons and the same *net* charge, although the formal charges of individual atoms may vary among the various Lewis structures. The number of valence electrons cannot change.	The Lewis structures  and  H I are *not* resonance forms of one another. Structure H has 24 valence electrons and a net charge of 0; I has 26 valence electrons and a net charge of −2.
6. Each contributing Lewis structure must have the same number of *unpaired* electrons. And each resonance structure must also have the same number of bonds	Structural formula J is a Lewis structure of nitromethane; K is not, even though it has the same atomic positions and the same number of electrons.  and  J K Structure K has 2 unpaired electrons. Structure J has all its electrons paired and is a more stable structure.
7. Electron delocalization stabilizes a molecule. A molecule in which electrons are delocalized is more stable than implied by any of the individual Lewis structures that may be written for it. The degree of stabilization is greatest when the contributing Lewis structures are of equal stability. By delocalizing electrons they are "spread out" and given greater separation, minimizing their mutual repulsion.	Nitromethane is stabilized by electron delocalization more than methyl nitrite is. *The two most stable resonance forms of nitromethane are equivalent to each other.*  *The two most stable resonance forms of methyl nitrite are not equivalent.*  $CH_3-\ddot{\underset{..}{O}}-\ddot{N}=\ddot{O}: \longleftrightarrow CH_3-\overset{+}{\ddot{O}}=\ddot{N}-\ddot{\underset{..}{O}}:^-$

PROBLEM 1.16 Electron delocalization can be important in ions as well as in neutral molecules. Using curved arrows, show how an equally stable resonance structure can be generated for each of the following anions:

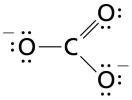
(a)



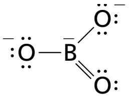
(b)



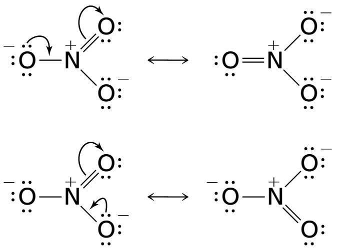
(c)



(d)



SAMPLE SOLUTION (a) When using curved arrows to represent the reorganization of electrons, begin at a site of high electron density, preferably an atom that is negatively charged. Move electron pairs until a proper Lewis structure results. For nitrate ion, this can be accomplished in two ways:



Three equally stable Lewis structures are possible for nitrate ion. The negative charge in nitrate is shared equally by all three oxygens.

It is good chemical practice to represent molecules by their most stable Lewis structure. The ability to write alternative resonance forms and to compare their relative stabilities, however, can provide insight into both molecular structure and chemical behavior.

from Carey, *Organic Chemistry*